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## DESCRIPTION

### 1. TITLE

Organic materials with non-linear optical properties and a process for their manufacture.

### 2. WHAT IS CLAIMED IS:

1. Organic materials with non-linear optical properties, characterized in that there is formed onto a thin film of a solid phase polymerizable aliphatic<sup>1</sup> diacetylene, which has been able to form a crystalline macromolecule by solid phase polymerization, laminated layers of molecules having a benzene ring framework, which is a  $\pi$ -electron conjugated system, with its two ends having an electron-donating group and an electron-accepting group.

2. Organic materials with non-linear optical properties, characterized in that there is formed, by a vacuum deposition process, onto a thin film of a solid phase<sup>2</sup> polymerizable aliphatic diacetylene, which has been able to form a crystalline macromolecule by solid phase<sup>3</sup> polymerization, layers of molecules having a benzene ring framework, which is a  $\pi$ -electron conjugated system, with its two ends having an electron-donating group and an electron-accepting group.

### 3. BACKGROUND OF THE INVENTION

#### (Industrial Field)

The invention relates to thin films of materials with non-linear optical properties and to a process for their manufacture.

(Description of the Related Art)

Organic compounds having electron-donating and electron-accepting groups interacting via a  $\pi$ -electron conjugated system are receiving attention as materials with non-linear optical properties from the viewpoints that they exhibit very much greater non-linear optical properties than inorganic compounds and organic compounds and also that they have the potential for comparatively free molecular designs.

However, it is necessary to orient these organic molecules and make them crystalline, in order to use these non-linear optical materials for practical devices which will produce non-linear optical properties, such as second harmonics, in large amounts. The conventional Langmuir-Blodgett (LB) process is already known as a process for the formation of thin oriented organic films. This process is characterized in that an organic molecule having, on the one hand, hydrophilic groups and, on the other hand, hydrophobic groups, deployed in a unimolecular form on a water surface, is in a condition whereby the organic molecule is standing perpendicularly on the water surface and is accumulated onto a suitable substrate: it is usually possible to obtain thin films in which the axes of the organic molecules are oriented in a direction perpendicular to the substrate.

However, there are the following restrictions on the organic molecules used in the LB process. Firstly, in order to express the orientation effectively using this process, it is

necessary to carry out design and synthesis such that there is a balance between the hydrophilic and hydrophobic groups at the two ends of the organic molecule being used, which has long chain alkyl groups frameworks. Also the long chain alkyl groups extend over a few tens of ångströms, so that weak structural interactions at the two ends are not prevented. Furthermore, it cannot be disregarded that there are restrictions on the materials, in order for the manufacturing stages to be wet processes and that it takes much time to make a specified thickness, so that there is formation of a uni-molecular layer.

As well as the Langmuir-Blodgett process, there is also the vacuum deposition process for forming thin films. The vacuum deposition process is a dry process and it has recently become the general process for forming thin films of organic compounds. However, it is generally not easy to control the orientation of the molecules in this vacuum deposition process. This is a major problem when it is a result of the situation that it is impossible to select combinations of substrates for forming thin films and film substances whose crystal structures and lattice constants are closely similar, as is the case when there are Group IV semiconductors, compound semiconductors or inorganic compounds in general.

In order to solve this, there are processes for controlling the orientation of deposited organic molecules by using, for example, uniaxially stretched oriented polyester films as substrates, but the degree of orientation is low.

(Problems to be solved by the invention)

As described in the previous Section, the common problem presented with the related art is that it is difficult to obtain the substrates needed for the formation of the thin films, when good quality thin crystalline films are formed by either of the thin film-forming processes, the LB process or the vacuum deposition process. The purpose of the invention is to provide thin films of organic materials with non-linear optical properties, whose vacuum-deposited organic molecules are oriented to a high degree and whose non-linear optical properties are large, by using, as substrates for vacuum deposition, substrates comprising organic macromolecular materials whose affinity with vacuum deposited organic molecules is high and which are highly crystalline and highly oriented, without the substrates being formed from inorganic molecules, which have greatly differing chemical properties and geometric shapes, while using the vacuum deposition process, which is a practical means of thin film formation.

(The Means of Solving the Problems)

The invention, in order to realize the aforementioned purpose, is constructed from:

1. Organic materials with non-linear optical properties, characterized in that there is formed onto a thin film of a solid phase polymerizable aliphatic diacetylene, which has been able to form a crystalline macromolecule by solid phase polymerization, laminated layers of molecules having a benzene

ring framework, which is a  $\pi$ -electron conjugated system, with its two ends having an electron-donating group and an electron-accepting group and

2. Organic materials with non-linear optical properties, characterized in that there is formed, by a vacuum deposition process, onto a thin film of a solid phase polymerizable aliphatic diacetylene, which has been able to form a crystalline macromolecule by solid phase" polymerization, layers of molecules having a benzene ring framework, which is a  $\pi$ -electron conjugated system, with its two ends having an electron-donating group and an electron-accepting group.

(Effects)

That is, it is recalled that, according to the invention, thin films of organic materials with non-linear optical properties can be provided, by laying down layers of deposited molecules oriented in a set direction, using solid-phase polymerizable aliphatic diacetylene compounds, from which highly crystalline thin films can be obtained, as substrates and using, as the deposited molecules, molecules having an aforementioned  $\pi$ -electron conjugated system, whose two ends have an electron-donating group and an electron-accepting group.

It is possible to prescribe the direction of orientation of the deposited molecules by using as a substrate, a thin film comprising an aliphatic diacetylene which has been able to polymerize in the solid phase, but the molecules have a different orientation from the direction perpendicular to the



substrate arising from the Langmuir-Blodgett process and the orientation of the molecules has the potential to be controlled by the functional groups used in the side chains of the aliphatic diacetylenes used as substrates according to the invention.

The solid phase polymerizable aliphatic diacetylene compounds according to the invention have aliphatic functional groups at the two ends of the diacetylenes and are readily polymerized in the solid phase by heat or light, especially ultraviolet light, and the formation of crystals is targeted. The reactivity, for example, the rate of polymerization, of a diacetylene is known to be regulated in general by the types and sizes of side chain functional groups, but the crystallinity, on the other hand, depends on the chemical nature of the side chain functional groups. The chemical formulae of the aliphatic diacetylene compounds may generally be written as  $R-C\equiv C-C\equiv C-R'$  and desirable specific embodiments have  $R = -(CH_2)_nCH_3$ ,  $R' = -CH_2OH$ ,  $-(CH_2)_nCOOH$ ,  $-(CH_2)_nOCONH(CH_2)_mCH_3$ , or  $R = R' = -(CH_2)_nOH$ ,  $-(CH_2)_nOCONH(CH_2)_mCH_3$  or the like. The length and size of these side chain functional groups influence the size of the macromolecular crystal lattices and the  $-OH$  group and the urethane group  $-OCONH-$  act as important factors in controlling the degree of crystallinity of the macromolecular crystals, due to their participation in the formation of intra- and inter-molecular hydrogen bonds. The thicknesses of the films of these solid phase polymerizable aliphatic diacetylenes, which are used as molecular substrates for deposition, are not

especially limited. These diacetylenes which are used as substrates may be employed adhered to quartz glass, compounds which are semiconductors, or metals, in order to bond them to optical elements. The formation of the substrate may either be by coating a solution, or by a deposition process. From the viewpoint of uniformity and the like, a deposition process is desirable, but, where there are accompanying difficulties, for example, from thermal decomposition, there may naturally be coating from a solution.

A description will next be given of the non-linear organic deposition molecules, in which the electron-donating and electron-accepting groups at the two ends interact via the  $\pi$ -electron conjugated systems.

The  $\pi$ -electron conjugated systems used according to the invention are desirably benzene, 1,2-diphenylethylene, 1,2-diphenylacetylene and 1,4-diphenyldiacetylene. The electron-donating groups may typically be: amino groups; N-alkylamino groups, typified by N-methylamino groups; N,N-dialkylamino groups, typified by N,N-dimethylamino groups; hydroxyl groups and alkoxy groups. Examples of the electron-accepting groups which may be given are: nitro groups, cyano groups, thiocyno groups, aldehyde groups, carboxyl groups and carbonyl groups.

Specific embodiment compounds which may be given, without the invention being especially limited to these compounds, are the compounds termed: meta- and para- nitroanilines, 2-methyl-4-

nitroaniline, 1 [4' N,N'-dimethylaminophenyl]-4-(4"-nitrophenyl)diacetylene, *meta*-dinitrobenzene, 2-bromo-4-nitroaniline, formylnitrophenylhydrazine and nitro-4-phenyl-N-(methylcyano-methyl)amine.

The deposition process for the molecules being deposited according to the invention is not especially limited, but, in order to express the orientation and optical properties well, it is desirable to have the thicknesses of the deposited films approximately 100 Å to 10 µm. It is undesirable to have markedly high temperatures for the deposition: this avoids decomposition of the organic compounds.

(Examples)

The invention will be explained concretely below by means of examples of its execution.

Table 1 lists the names, chemical formulae, formation processes, formation temperatures and film thicknesses of the solid phase polymerizable aliphatic diacetylenes used.

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Table 1

Name	Chemical Formula	Formation Process	Formation Temperature	Film Thickness
4,6-Decadiyne-1,10 diol	$R-C\equiv C-C\equiv C-R$ $R = (CH_2)_8-OH$	Vacuum deposition	$110^\circ \pm 10^\circ C$	400 Å
Tricosa-(10,12)-diynoic acid	$R-C\equiv C-C\equiv C-R'$ $R = (CH_2)_8-CH_3$ $R' = (CH_2)_8-CO_2H$	Vacuum deposition	$50^\circ \pm 10^\circ C$	400 Å
Diacetylene-4-butoxy <sup>22</sup> carbon-ylmethylethane	$R-C\equiv C-C\equiv C-R$ $R = (CH_2)_8-OCONHCH_2OCOC_4H_9$	Vacuum deposition	$>120^\circ C$	400 Å

These were all formed onto quartz glass. After forming each substrate, polymerization in the solid phase was promoted by irradiation with ultraviolet light, using a 200 W mercury lamp in air. The crystallinity of each polydiacetylene sample was ascertained using X-ray diffraction when the solid phase polymerizations were finished. Just the (0, 2n, 0) reflections were observed for each material: the powdered raw materials showed clearly different orientation properties.

Using each of these solid phase polymerizable aliphatic polydiacetylene crystalline thin films as substrates, 2-methyl-4-nitroaniline (MNA), which is an organic material with non-linear optical properties, was vacuum deposited at  $2 \times 10^{-5}$  torr. The substrate temperature was room temperature and the

raw material temperature was 90°C. The thicknesses of the 2-methyl-4-nitroaniline films deposited were 500 to 2000 Å.

The orientation of the crystals of 2-methyl-4-nitroaniline deposited on the crystalline macromolecular thin films were evaluated by means of X-ray diffraction. For comparison, the 2-methyl-4-nitroaniline organic material with non linear optical properties was vacuum deposited onto a substrate of untreated quartz glass, which had not had a solid phase polymeric polyacetylene described according to the invention deposited or coated onto it and this was appraised by means of X-ray diffraction. The results are given in Table 2.

Table 2

Number	Name	Compound Deposited	Degree of Orientation of Compound Deposited*
1	4,6-Decadiyne-1,10-diol	2-Methyl-4-nitroaniline	>5
2	Tricosa-(10,12)-diynoic acid	2-Methyl-4-nitroaniline	>5
3	Diacetylene-4-butoxy <sup>14</sup> carbonyl-methylurethane	2-Methyl-4-nitroaniline	>5
4	Quartz glass	2-Methyl-4-nitroaniline	2

\*The degree of orientation is defined as the ratio of the (11 $\bar{2}$ ) diffraction intensity to (020) diffraction intensity obtained by X-ray diffraction.

Here the strength of the (11 $\bar{2}$ ) reflection shows how closely parallel the 2 methyl-4-nitroaniline molecular surface is to the polydiacetylene crystalline thin film substrate and the strength of the (020) reflection expresses the density of the

2-methyl-4-nitroaniline, which is in the condition that the molecular surface is oriented perpendicularly to the substrate surface. In the process according to the invention, it is possible to realize positioning whereby the molecular surface has an orientation parallel to the substrate, unlike the Langmuir-Blodgett process, where the positioning of the molecules is perpendicular to the substrate. It was discovered that these trends are clearly increased with solid phase polymerizable aliphatic diacetylene crystalline thin film substrates.

(Effects of the Invention)

It is possible to orient molecules of  $\pi$ -electron conjugated systems having electron-donating and electron-accepting groups at their two ends in a set orientation, by depositing these molecules onto a substrate comprising crystalline deposits or crystalline coatings of solid phase polymerizable aliphatic polydiacetylenes according to the invention.

Representative: Patent Attorney T. Sugiyama (1 other person)

## Translator's Report/Comments

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In translating the above text we have noted the following apparent errors/unclear passages which we have corrected or amended:

Page/para/line*	Comment
	<ol style="list-style-type: none"><li>1. Throughout this Specification, the description "aliphatic diacetylenes" refers to diacetylenes substituted with aliphatic groups as described on page 7 of this translation.</li><li>2. The Japanese says "inherently".</li><li>3. The Japanese says "intrinsic".</li><li>4. The Japanese says "solid layer polymerization".</li><li>5. The Japanese says "Byfoxy".</li></ol>

\* This identification refers to the source text. Please note that the first paragraph is taken to be, where relevant, the end portion of a paragraph starting on the preceding page. Where the paragraph is stated, the line number relates to the particular paragraph. Where no paragraph is stated, the line number refers to the page margin line number.

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